AFOSR-TR- 87-0051

RF Project 764977/717636
Annual Report

STRENGTH AND STRUCTURE OF $Ga_{1-x}In_x$ AS ALLOYS

Sponsored by

Advanced Research Project Agency (DOD)

ARPA Order No. 5526

Monitored by AFOSR Under Contract # F49620-85-C-0129

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October 31, 1986

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SECURITY CLASSIFICATION OF THIS PAGE

ADA177180

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR.TR. 87-0051
6a. NAME OF PERFORMING ORGANIZATION The Ohio State University Research Foundation 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR
6c. ADDRESS (City, State and ZIP Code) 1314 Kinnear Road Columbus, Ohio 43212	7b. ADDRESS (City, State and ZIP Code) Dept. of the Air Force Bolling AFB DC 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR 8b. OFFICE SYMBOL (If applicable) NE	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. F49620-85-0129
8c. ADDRESS (City, State and ZIP Code) Same as 7B	10. SOURCE OF FUNDING NOS. PROGRAM ELEMENT NO. 61102F 2917 / PROJECT NO. 5526 A3 / TASK NO. 00 / WORK UNIT NO. DARPA
11. TITLE (Include Security Classification) Strength and Structure of $GA_{1-x}IN_xAs$ Alloys	
12. PERSONAL AUTHOR(S) Katherine T. Faber and John Hirth	
13a. TYPE OF REPORT Annual 13b. TIME COVERED FROM 9/1/85 TO 8/31/86	14. DATE OF REPORT (Yr., Mo., Day) October 31, 1986 15. PAGE COUNT 38
16. SUPPLEMENTARY NOTATION	
17. COSATI CODES FIELD / GROUP / SUB. GR.	18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Gallium Arsenide, Indium Arsenide

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Substantial solid solution strengthening of GaAs by In acting as InAs units has recently been predicted for an intermediate temperature, plateau region. This strengthening could account, in part, for the reduction of dislocation density in GaAs single crystals grown from the melt. A high temperature hardness tester was designed and constructed for use to 900°C. Measurements have been carried out on (100) GaAs, $Ga_{0.9975}In_{0.0025}As$ and $Ga_{0.99}In_{0.01}As$ wafers, all of which contain small amounts of boron. Results show a significant strengthening effect in In-doped GaAs. A nominally temperature-independent flow stress region is observed for all three alloys. The In-doped GaAs shows a higher plateau stress level with increasing In content, consistent with the solid solution hardening is sufficient to explain the reduction in dislocation density with In additions. Electron microscopy is used to interrelate the mechanical properties of these alloys to their dislocated structures.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Captain Kevin Malloy	22b. TELEPHONE NUMBER (Include Area Code) 202-767-4933 22c. OFFICE SYMBOL Electronic and Material Sciences NE

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

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Report Summary

A. Technical Problem

In recent years, it has been noted that minute additions of indium (on the order of 1%) to gallium arsenide grown form the melt greatly reduces the dislocation density to levels of less than 10^2 cm/cm^3. [1] The mechanism by which this phenomenon occurs has been speculated to be solid solution strengthening, in which In together with its four nearest neighbor As atoms acts as the hardening unit. [2] In order to verify this strengthening mechanism, a program has been undertaken to determine the strength of $Ga_{1-x}In_xAs$ alloys as a function of temperature and composition. Electron microscopy is also used to interrelate the mechanical properties to their dislocated structures.

B. General Methodology

The basis of the solid solution strengthening in GaAs by indium additions is developed from the work of Mikkelson and Boyce. [3] They studied bond lengths in the Ga-In-As system by EXAFS and showed that the overall lattice parameter increases linearly with In concentration in accordance with Vegard's law. However, the Ga-As and In-As bond lengths remains roughly constant with In concentration. This indicates that each In atom, together with its four nearest As neighbors, acts as a center of strain analogous to a solute atom in a metal. Specific calculations based upon bond length changes suggest that the $InAs_4$ unit produces a local dilatation of 21%, considered to be a moderately strong solution hardener by metallic standards. [2]

In a solid solution strengthening model, dislocations bow out in their glide planes between solute "pins", the strength of the pinning being proportional to the magnitude of the dilatational strain (in this case

21%). The theory predicts that at low temperatures, the strength varies with the square root of the solute concentration. The more important effect, however, occurs with increasing temperature where a temperature independent "plateau stress" is observed compared to the pure solute which may extend to an appreciable fraction of the melting point. An increase in relative strengthening should be observed with temperature.

The experiments used to study solid solution strengthening in $Ga_{1-x}In_xAs$ alloys consists firstly of Vickers microhardness measurements as a function of temperature. Since the yield stress of a material is approximated by one-third of its hardness, the microhardness is a good "first cut" to examine if these materials exhibit a plateau stress associated with solid solution hardening. These experiments required the construction of a hot hardness tester, described in detail in Appendix A.

In addition, compression testing as a function of temperature is used to determine the critical resolved shear stress directly from the stress-strain curve. This particular test, though more difficult to conduct than hardness tests, supersedes the problem of surface degradation which is present in the hot hardness tests at elevated temperatures. In these tests, bulk mechanical properties are measured while the surface is protected in a bath of B_2O_3 to prevent As volatilization. These tests required the purchase of a high temperature furnace such that deformation mechanisms near the melting point of GaAs could be studied.

Electron microscopy of the dislocation structures of undeformed and deformed materials is a necessary part of this study. Solid solution hardening by pinning requires that the dislocation configuration to be of the smoothly-bowed, line tension type. However, if dislocation motion occurs by double-kink nucleation and growth, the deformed materials would

contain straight dislocations. By electron microscopy, it will then be possible to differentiate the operative mechanisms in solid solution hardening.

C. Technical Results

Results of the hardness tests are shown in Figure 1 and described in greater detail in Appendix B. The hardness is related to the critical resolved shear stress by the following relationship:

$$\sigma_{CRSS} = 0.5\ (H/3)$$

where 0.5 is an upper bound estimate of the Schmid factor which incorporates the vectors for transforming coordinate systems between the tensile axis and the slip plane. The critical resolved shear stress data obtained from hardness data is shown in Figure 2. Note also on this graph is a comparison with undoped Bridgeman crystals studied by Swaminathan and Copley [4] and undoped and and In-doped LEC crystals by Tabache [5] determined from lower yield strength measurements.

Extrapolation of our data to the melting point of GaAs allows comparison with the calculated thermal stresses developed during the LEC growth process. Note that the results suggest that crystals highly doped in In have sufficient solid solution hardening to prevent yielding and the accompanying dislocation generation.

Initial studies are currently underway to resolve the difference between the present results and the compression test results of Swamanathan and Copley and Tabache. One potential explanation was that the enhanced CRSS is associated with the presence of boron. Boron, an isoelectronic substitute for Ga, could be a strong solid solution hardener if it is distributed uniformly. Recent hardness measurements on GaAs containing 1 ppm boron and 0.1 ppm boron (compared to 7-9 ppm boron in the original

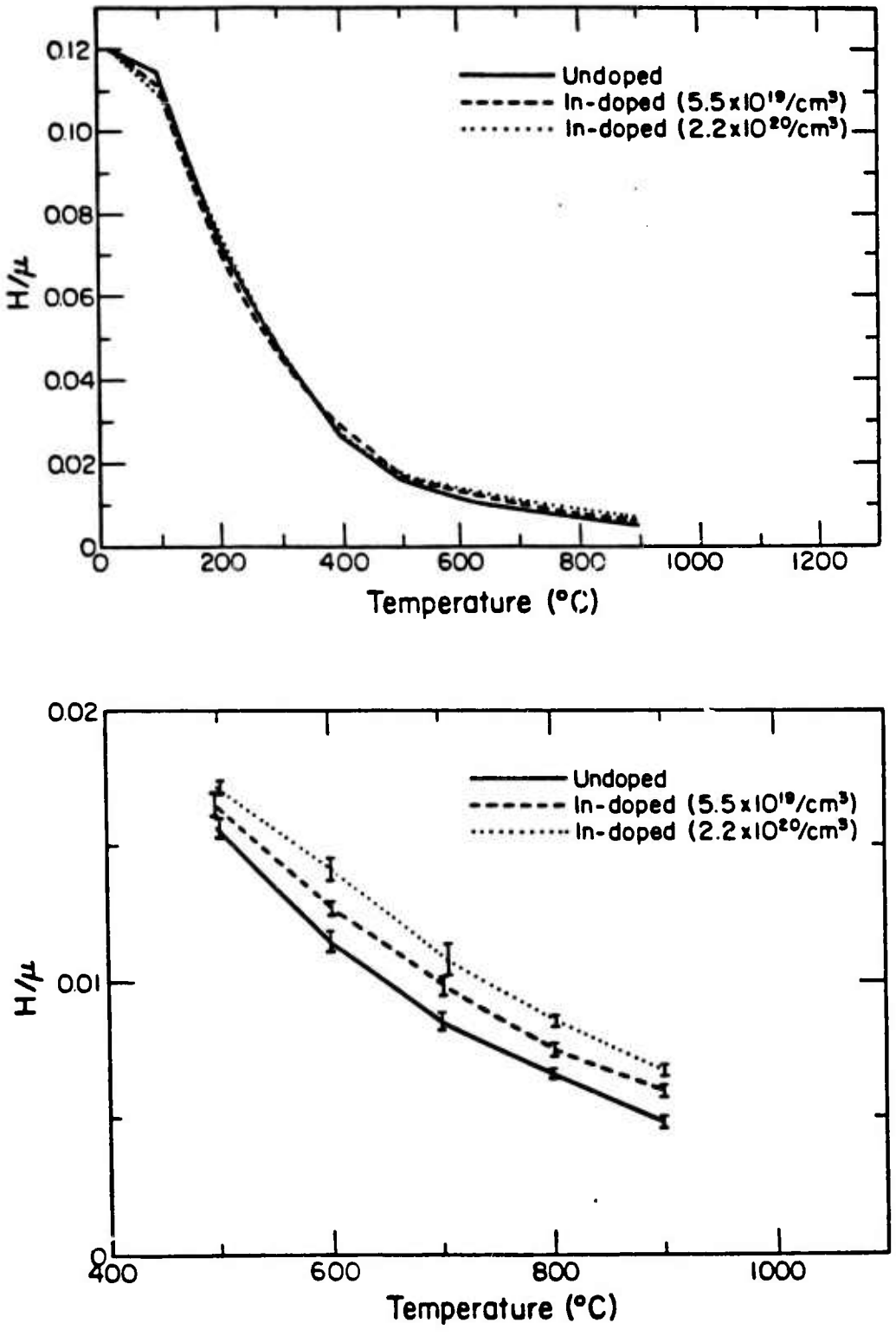


Figure 1. Normalized hardness versus temperature for GaAs, $Ga_{.9975}In_{.0025}As$, and $Ga_{.99}In_{.01}As$.

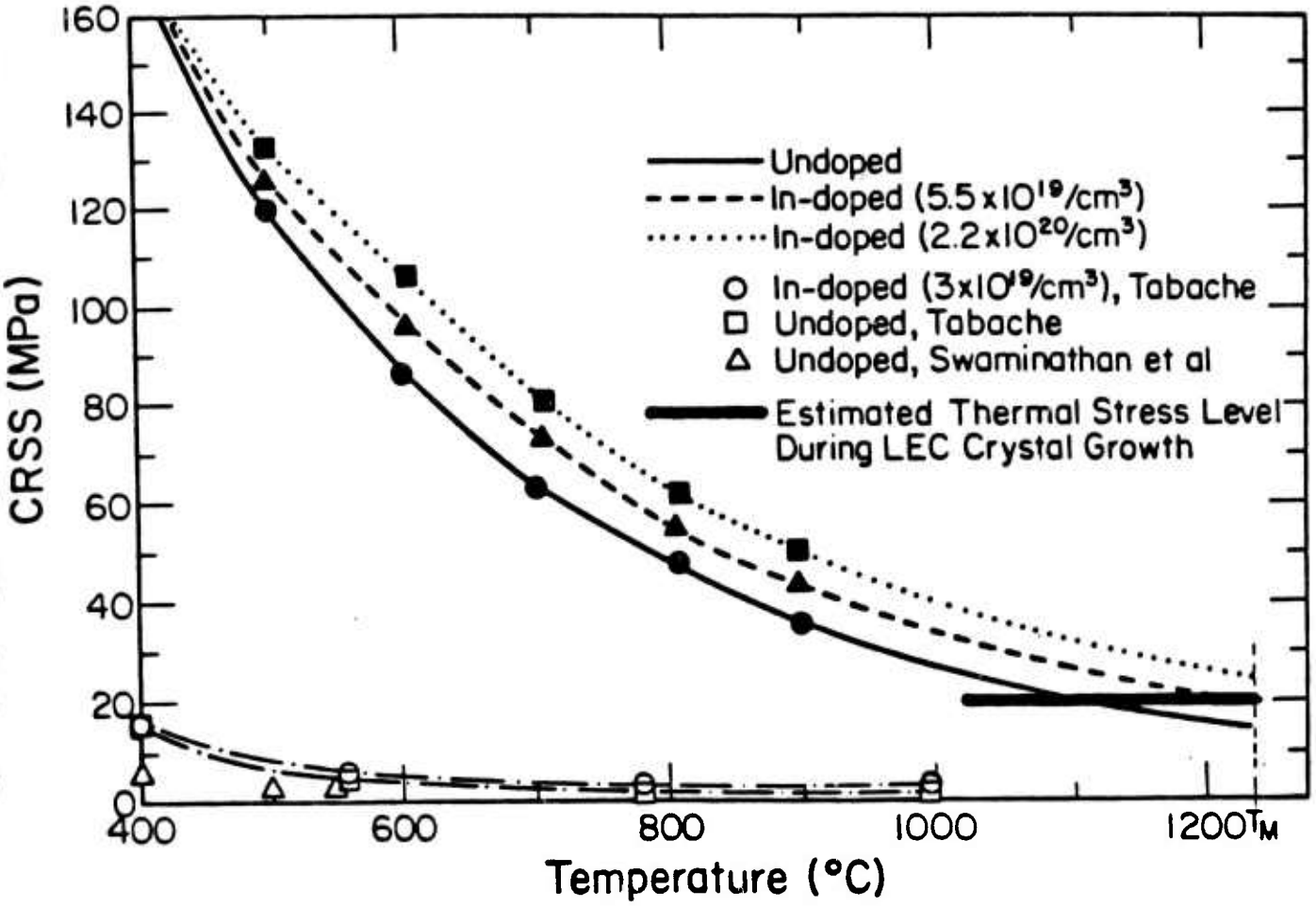


Figure 2. Critical resolved shear stress estimated form hardness data compared with the compression test data of Swaminathan and Copley [4] on undoped GaAs and Tabache [5] on undoped and In-doped LEC GaAs.

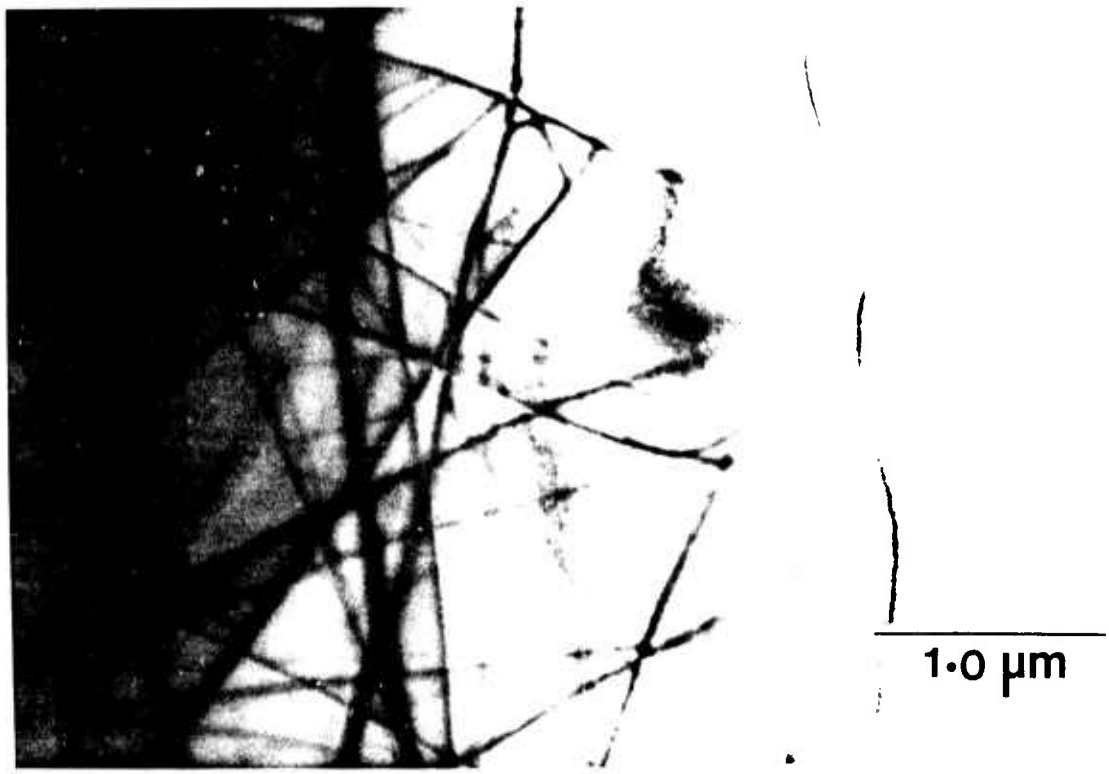
materials) indicate that boron is not responsible for the discrepancy between the data sets. An alternative suggestion will be discussed in the following section.

Studies of dislocations in undoped and In-doped alloys are being performed by transmission electron microscopy using a JEOL JEM 200CX. Figure 3 shows the bright field image of [100] undoped GaAs along with the selected area electron diffraction pattern. Dislocation networks are clearly visible in the micrograph. Dark field images were also taken using different reflections for characterizing these dislocations. Applying $\vec{g}\cdot\vec{b}$ criteria from different dark field images, some of the dislocations were found to have a Burgers vector of the type 9/2<011>. Figure 4 shows the bright field electron micrograph in the case of [100] $Ga_{0.9975}In_{0.0025}As$. Some straight dislocations are clearly seen in the image but their density is clearly less than the undoped material. In order to understand the role of the In-doping in reducing dislocation density, a detailed study by conventional transmission microscopy and high resolution transmission electron microscopy is in progress.

D. Implications for Future Research

Compression testing of undoped and In-doped (100) single crystals will be carried out at temperatures of 700 to 1100°C at a strain rate of 10^{-4}/s in the <100> orientation where multiple slip systems operate. Further tests are also planned for the <123> (single slip) and <112> (dual slip) orientations. Hardness measurements comprise multiple slip conditions, as do the thermally-derived stresses in the LEC growth process. Hence, it is expected that compression measurements in the <100> orientation are comparable to growth conditions. Previous work has been conducted on GaAs in the single slip configuration [5] or at low temperatures (<550°C) in the

(a)



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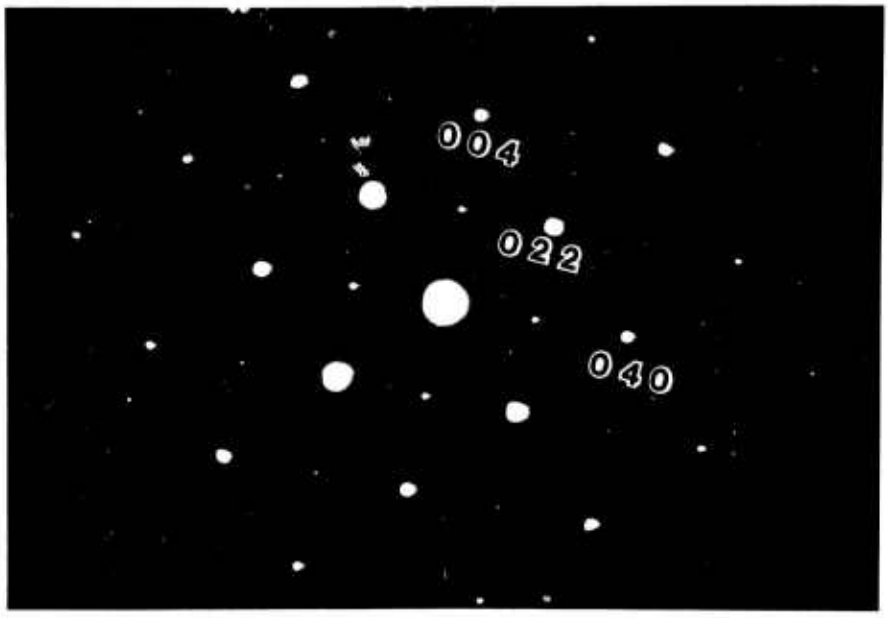

Figure 3. (a) Transmission electron micrograph of GaAs. (b) Selected area electron diffraction pattern of GaAs.

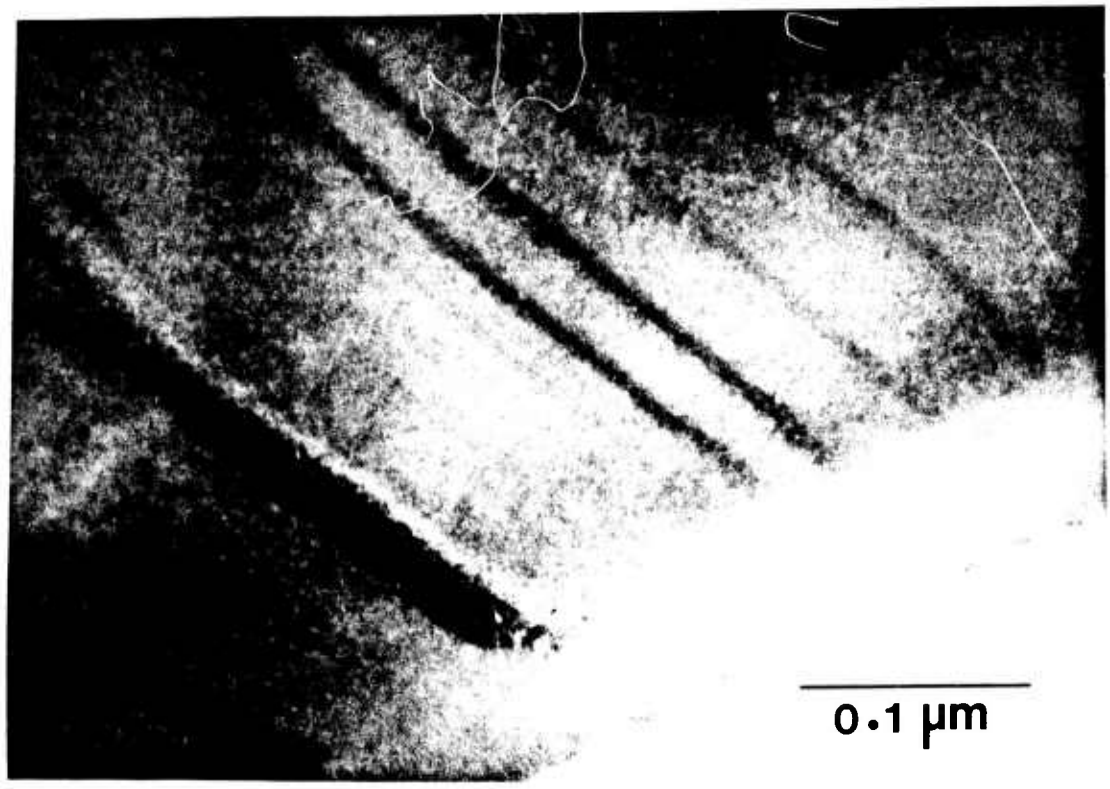

Figure 4. Transmission electron micrograph of $Ga_{0.9975}In_{0.0025}As$.

multiple slip configuration [4], and thus, may explain the large difference in the critical resolved shear stresses obtained.

Etch pit studies and transmission electron microscopy of the deformed crystals will be continued. The information on dislocation type, distribution and nature of dislocation pinning obtained from transmission electron microscopy examination and critical resolved shear stress obtained from compressive tests should enable us to identify the mechanism of dislocation density reduction in In-doped GaAs crystals.

In addition to work of the III-V system, it is of interest to pursue similar studies in II-VI systems which potentially demonstrate enhanced mechanical properties by addition of a third isoelectronic species. One candidate is the $Cd_{1-x}Mn_xTe$ system. Compositions across the CdTe-MnTe binary can be supplied by Prof. Jack Furdyna of the University of Notre Dame. Such studies would be particularly interesting in lieu of the predictions of solid solution strengthening made by Hirth and Ehrenreich in II-VI systems.[6]

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APPENDIX A

MECHANICAL PROPERTIES OF $Ga_{1-x}In_xAs$

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ABSTRACT

Substantial solid solution strengthening of GaAs by In acting as $InAs_4$ units recently been predicted. This strengthening could account for the reduction of dislocation density in GaAs single crystals grown from the melt. High temperature hardness measurements up to 700°C have been carried out on (100) GaAs and $Ga_{0.9975}In_{0.0025}As$ wafers. Results show a significant strengthening effect in In-doped GaAs even at concentration levels of about 0.2 wt%. A temperature independent flow stress region is observed for both these alloys. The In-doped GaAs shows a higher plateau stress level compared to the undoped GaAs. The results are consistent with the solid solution strengthening model.

INTRODUCION

Addition of a few percent indium to GaAs melt has been known to reduce the dislocation density in single crystals grown by the Czochralski process to levels of <100 cm/cc [1]. It has been proposed that this effect may be explained by the solid solution strengthening of GaAs at elevated temperatures by In [2]. Solute atoms distort the solvent lattice because of the difference in size. The elastic stress field caused by this distortion interacts to first order with the elastic field of dislocation. This impedes the dislocation motion and therefore increases the flow stress of the host lattice. Differences in elastic modulus and valence have a second order influence on the resistance to dislocation motion. In $Ga_{1-x}In_xAs$, $InAs_4$ tetrahedral cluster is considered to be the solute unit that causes strengthening (Figure 1).

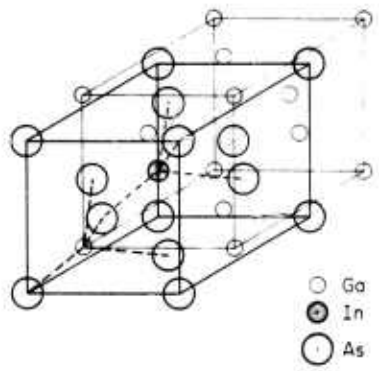

Figure 1. $Ga_{1-x}In_xAs$ lattice and $InAs_4$ solute unit.

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EXAFS studies by Mikelson and Boyce [3] show that in the Ga-In-As system, the overall lattice parameter varies linearly with In concentration in accordance with Vegard's law, while the Ga-As and In-As bond lengths are essentially the same as in the corresponding pure crystals (Figure 2). Ehrenreich and Hirth inferred [2] that each In atom together with its four nearest As neighbors acts as a center of strain analogous to a solute atom in a metal. Substitution of Ga by In thus causes a volume dilatation of about 21% and an associated tetrahedral strain field. This is a large strengthening effect for a substitutional solute compared to most metallurgical systems[4].

As in the case of solution strengthened metals [4], a temperature independent flow stress (plateau stress) extending to an appreciable fraction of the melting point is expected for Ga-As with In additions. The plateau stress level should increase with In content.

This work concerns the experimental measurement of the flow stress and hardness as a function of temperature and In content. High temperature hardness testing is used to estimate the influence of indium on strength and confirm the existence of the plateau-stress. The yield stress level is approximately 1/3 of the hardness value so the latter indicates expected trends for yield stress.

EXPERIMENTAL WORK

Figure 3 shows the hardness tester designed and fabricated for high temperature hardness measurements. The loading is applied by dead weights with a counterbalance arrangement to vary the load from 10 to 300 gms.

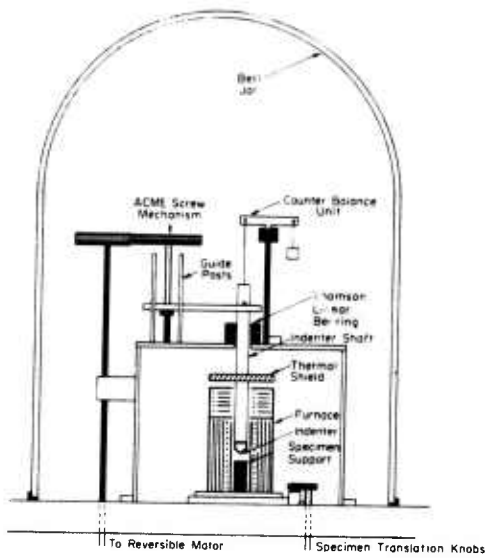

Figure 3. High temperature hardness tester used in this study.

The indenter is raised and lowered at a constant rate of about 3 mm/minute by a screw mechanism. The furnace used is a low heat capacity Pt-20%Rh resistance wire-wound unit capable of fast heating and cooling rates and a maximum temperature of 1500 °C. Ultra high purity argon, flowing into the enclosure, is used to cool the upper part of the indenter shaft. All indentation measurements are made at room temperature.

Vickers hardness measurements on a (100) GaAs wafer and a (100) $Ga_{0.9975}In_{0.0025}As$ wafer (obtained from Westinghouse R&D Center) were made over a temperature range of room temperature to 900°C. Indentations were made during heating and cooling and compared to ensure that no significant change in dimensions of the indentation diagonals had occured when the specimen was taken to the higher temperature. The indium content was confirmed by atomic absorption spectroscopy.

RESULTS AND OISCUSSION

Figure 4 shows the hardness test results for GaAs and $Ga_{0.9975}In_{0.0025}As$ (100) wafers. Table 1 also summarises the hardness values for these two alloys. Indium additions result in significantly higher hardnesses than that of the undoped material above 300 °C consistent with a solid solution strengthening model. The hardness drops sharply with temperature and flattens out at higher temperatures. The latter temperature indepedent hardness region is indicative of the existence of the plateau stress region. By virtue of its higher hardness, the alloy containing In could be inferred to have a higher plateau stress level. The tests are to be extended to higher temperatures to examine trends as the crystal growth temperature is approached.

Table I. Hardness versus temperature data for (100) GaAs and $Ga_{0.9975}In_{0.0025}As$.

TEMPERATURE	HARONESS (GPa)	
°C	GaAs	$Ga_{0.9975}In_{0.0025}As$
25	5.82 ± 0.14	5.82 ± 0.17
100	5.52 ± 0.17	5.72 ± 0.27
200	3.50 ± 0.31	3.54 ± 0.23
300	2.23 ± 0.18	2.21 ± 0.19
400	1.20 ± 0.04	-
500	0.72 ± 0.02	0.85 ± 0.014
600	0.52 ± 0.01	0.58 ± 0.004
700	0.378 ± 0.015	0.446 ± 0.027

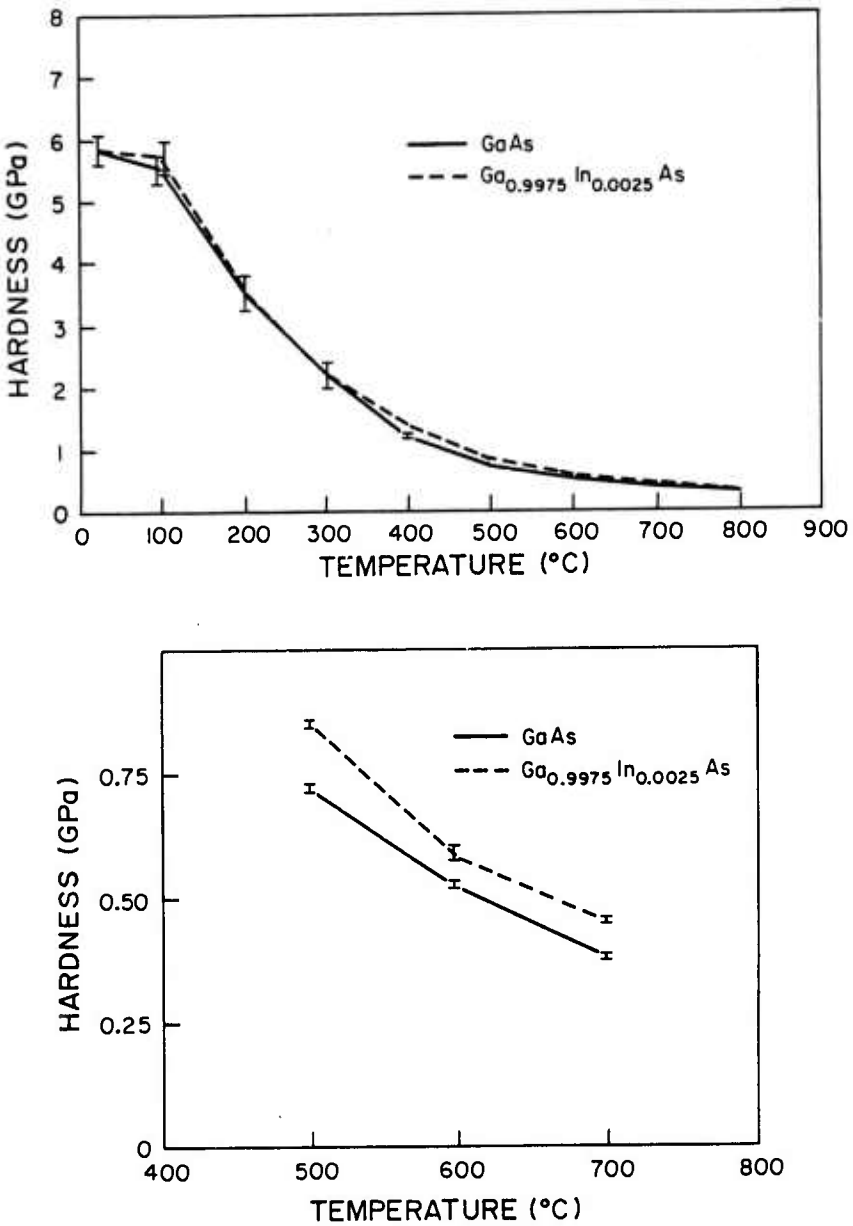

Figure 4. Hardness versus temperature for undoped GaAs and In-doped GaAs.

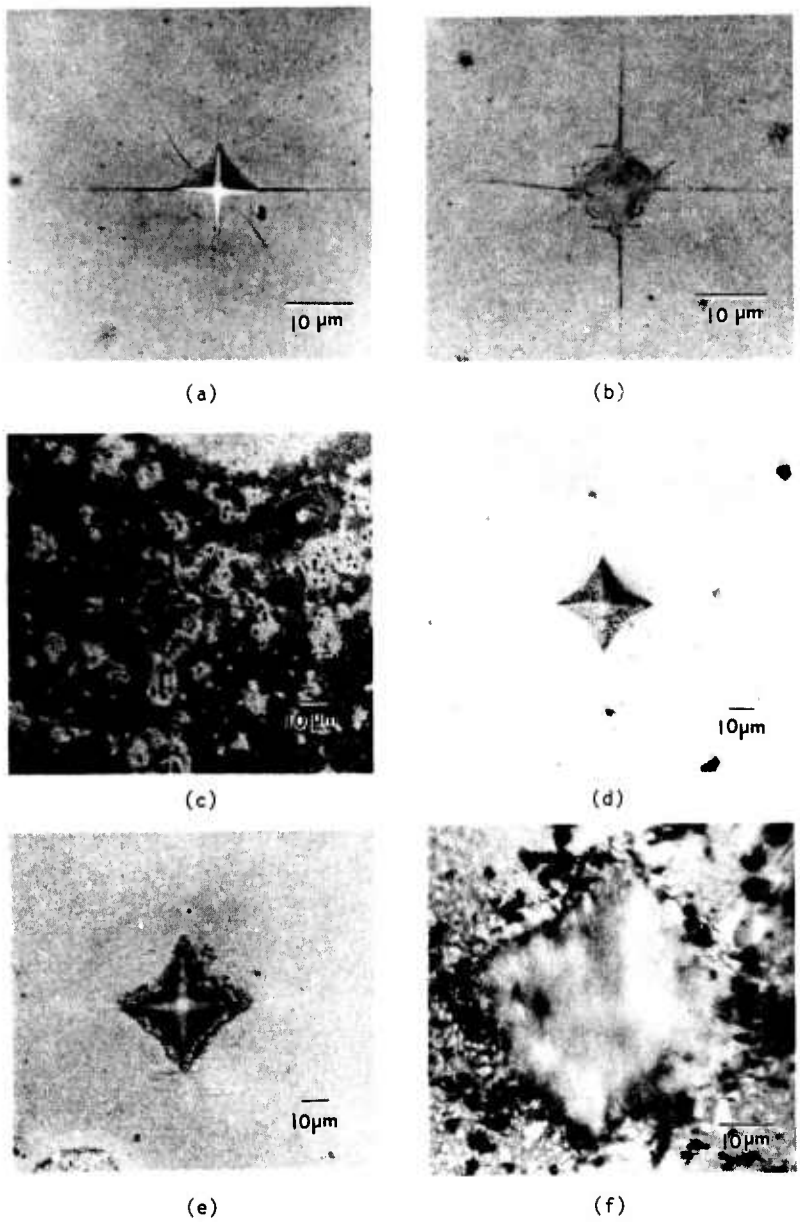

Figure 5. Optical micrographs of indentations made at different temperatures. (a) 25 °C, (b) 100 °C, (c) 300 °C, (d) 500 °C, (e) 700 °C and (f) 900 °C.

Figures 5a through 5f show the optical micrographs of the indentations made at 25, 100, 300, 500, 700 and 900 °C. Marked relaxation is seen in high temperature indentations; no cracks are are seen at indentation corners above 400 °C. This observation suggests that the ductile-to-brittle transition occurs betweer 300 and 400 °C. Above 700 °C, significant vaporization and surface damage is observed (Figure 5f). If tests are to be extended to higher temperatures, as mentioned earlier, the specimens need to be encapsulated with a thin protective film, e.g. silicon nitride.

Hardness tests do not provide information regarding the initial stages of deformation. This region of deformation is of primary concern, as dislocation densities of the order of 10^4 cm/cc could be generated at this stage. From the estimated thermal stress distribution in the ingot during crystal growth, a several fold increase in the critical resolved shear stress is expected with In additions. While the hardness data obtained thus far show a significant strengthening effect, it does not fully reflect the above expectation. Yield stress measurements under compressive loading are therefore necessary to obtain the details of the initial stage of deformation. Compressive yield strength measurements, together with transmission electron microscopy of the deformed crystals, will form the second phase of the experimental program.

SUMMARY

High temperature hardness test results show a significant strengthening effect of In in GaAs even at In concentration levels of about 0.2 wt%.

A temperature independent flow stress region is observed for both the alloys. The GaAs containing In shows a higher plateau stress level compared to GaAs with no In.

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ACKNOWLEDGEMENTS

This work was initiated under NSF PYI award (DMR-8351476) in conjunction with IBM, Champion Spark Plug Co., Eastman Kodak and Owens Corning Fiberglass. Current support is provided by AFOSR (Contract F49620-85-C-0129)

APPENDIX B

To appear in Journal of Applied Physics, December 1988

HIGH TEMPERATURE HARDNESS OF $Ga_{1-x}In_xAs$

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ABSTRACT

Substantial solid solution strengthening of GaAs by In acting as $InAs_4$ units has recently been predicted for an intermediate temperature, plateau region. This strengthening could account, in part, for the reduction of dislocation density in GaAs single crystals grown from the melt. Hardness measurements at high temperatures up to 900 ^oC, have been carried out on (100) GaAs, $Ga_{0.9975}$ $In_{0.0025}$ As and $Ga_{0.99}In_{0.01}As$ wafers, all of which contain small amounts of boron. Results show a significant strengthening effect in In-doped GaAs. A nominally temperature-independent flow stress region is observed for all three alloys. The In-doped GaAs shows a higher plateau stress level with increasing In content. The results are consistent with the solid solution strengthening model. The magnitude of the solid solution hardening is sufficient to explain the reduction in dislocation density with In addition.

INTRODUCION

Doping of GaAs with In in single crystals grown by the Czochralski process has been known to reduce the dislocation density from 10^3 - 10^4 cm/cc to $< 10^2$ cm/cc.[1] There is a consensus that the generation of dislocations in GaAs and other III-V compounds occurs when the thermal stress imposed on the crystal during growth exceeds the critical resolved shear stress (CRSS) of the crystal. While the minimization of thermal gradients, and hence, the stresses during growth are achieved by the control of process parameters such as B_2O_3 encapsulant height , cone angle, diameter control and ambient pressure, enhancing the inherent strength (CRSS) of the crystal is achieved by addition of isovalent dopants as well as other Group IV and VI elements. Of these, the isovalent In and the Group IV element Si have been found to be the most effective.[2] However In doping is desirable because of the minimal influence on the electrical behavior of the GaAs. The mechanism of dislocation density reduction at such low concentration levels of the dopant is yet to be resolved unequivocally. The drastic reduction in dislocation density suggests a very large increase in the strength with In doping. Thermal stress calculations suggest that the maximum stress experienced by the crystal is several times that of the extrapolated CRSS of an undoped GaAs crystal.[3] It has been suggested[4] that hardening akin to solid solution hardening occurs in GaInAs with an $InAs_4$ tetrahedral cluster being the solute unit that causes strengthening. EXAFS studies by Mikelson and Boyce[5] show that in the Ga-In-As system, the overall lattice parameter varies linearly with In concentration in accordance with Vegard's law, while the Ga-As and In-As bond lengths are

essentially the same as in the corresponding pure crystals. The interpretation of these results[4] is that each In atom together with its four nearest As neighbors acts as a center of strain analogous to a solute atom in a metal. Such a unit would cause a local tetrahedral strain field corresponding to a volume dilatation, $\delta V/V$, of about 21%. This large strain field should result in substantial solid solution strengthening in an intermediate temperature, plateau region. When the dislocations are pinned strongly by these strain centers, the increase in strength for an alloy containing 5×10^{19} atoms/cc of In is estimated to be about 120 %.

Generally compounds such as GaAs have strong temperature dependences for flow at low temperatures, corresponding to a rate controlling mechanism related to the intrinsic lattice resistance or Peierls' barrier. An athermal, plateau region appears at intermediate temperatures corresponding to extrinsic effects such as solid solution hardening, while at high temperatures other creep-type mechanisms would be applicable. The low temperature process consists of dislocation motion controlled by nucleation and lateral propagation of double kinks. With an increase in temperature, the nucleation and motion of double kinks occurs much more easily and the flow stress drops sharply (Figure 1). Misfit strain centers promote double kink nucleation while impeding the subsequent lateral propagation of the two kink segments.[6] The solute addition at low concentration levels could result in either hardening or softening depending on the magnitude of these opposing effects. However, the softening effect should be most prominant at the lowest temperatures where the double kink model is dominant and should

be less pronounced as the extrinsic athermal region is approached. Hence, a transition from softening to hardening with increasing temperature below the plateau region would be expected, analogous to observations for b.c.c. metals where the Peierls' mechanism is operative at low temperatures.[7]

In the athermal region beginning at about 700 ^{o}C for GaAs, double-kink nucleation no longer controls dislocation motion. In this region, the resistance to dislocation glide derives mainly from the interaction with solutes, and other defects such as intersecting dislocations and the dislocation motion occurs by breaking away from these pins. As in the case of solution strengthened metals,[8] a nominally temperature independent flow stress region would be observed. In actuality, the flow stress is not truly independent in the plateau region but the slope of the flow stress-temperature plot is significantly less in this region than at lower temperatures.[8] In this plateau region, the thermal component of flow stress is significantly less than the athermal component. The temperature-independent flow stress level (plateau-stress) would increase with increasing solute content. This region is expected to extend to a significant fraction of the melting temperature. Beyond this temperature, the flow stress would be determined by diffusion controlled deformation processes.

This work concerns the experimental measurement of the flow stress and hardness as a function of temperature and In content. High temperature hardness testing is used to estimate the influence of indium on CRSS and yield strength and to confirm the existence of the plateau-stress. The yield stress level is approximately 1/3 of the hardness

value[9] so the latter indicates expected trends for yield stress.

EXPERIMENTAL WORK

The hardness tester used in this study was designed and fabricated specifically for the testing of GaAs. Loading is applied by dead weights with a counterbalance arrangement to vary the load from 0.1 N to 3 N. The indenter is raised and lowered at a constant rate of 3 mm/minute by a screw mechanism. The furnace used is a low heat capacity Pt-20%Rh resistance wire-wound unit capable of rapid heating and cooling rates and a maximum temperature of 1500 ^{o}C. Ultra high purity argon, flowing into the enclosure, is used to cool the upper part of the indenter shaft. Hardness measurements were made from room temperature to 900 ^{o}C with a Vickers diamond pyramid indenter.

Testing was performed on (100) surfaces of wafers grown by the LEC method at Westinghouse Research and Development Center. Three compositions, undoped GaAs, $Ga_{0.9975}In_{0.0025}As$ and $Ga_{0.99}In_{0.01}As$, all semi-insulating, were studied. The concentration of In atoms in the above three alloys were 0, 5.5×10^{19} and 2.2×10^{20} atoms/cc. The indium content was confirmed by atomic absorption spectroscopy. All three alloys also contained boron at levels of 2×10^{18} atoms/cc. Boron contents were determined by spark source mass spectroscopy analysis at Battelle Columbus Laboratories. All hardness data are normalized by the shear modulus to give the residual temperature dependence related to the mechanisms. Data for the Voight average shear modulus were calculated from the anisotropic elastic constants given as a function of temperature by Jordan.[10]

RESULTS AND DISCUSSION

Figure 2 shows the hardness test results for GaAs, $Ga_{0.9975}In_{0.0025}As$ and $Ga_{0.99}In_{0.01}As$ (100) wafers. All data points represent the average of 10 hardness readings. The standard deviation for the sets of data are also shown for the high temperature region (Fig. 2b). Table 1 also summarizes the hardness values for these three alloys. As indicated in the figure, the hardening effect is significant relative to the scatter. A significant difference in hardness between undoped and In-doped GaAs is seen only above 300 °C. No cracks were observed at indentation corners above 400 °C. This transition from cracking to deformation by slip during indentation has also been observed in GaAs by other workers in the temperature range 300 - 400 °C.[11,12] However, these hardness studies were confined to temperatures less than 500 °C. The hardness drops sharply with temperature and flattens out at higher temperatures indicative of the existence of the plateau stress region. The shape of the curve is very similar to that observed for metals exhibiting plateau behavior.[8] By virtue of their higher hardness, the alloys containing In are inferred to have a higher plateau stress level. The increase in hardness compared to the undoped material is about 40% at 900 °C for the highly In doped alloy. Both the In-associated effects of the softening-hardening transition at low temperatures and the presence of the plateau region are consistent with the model discussed previously of Peierls' control superceded by solid solution hardening. The interpretation of the solid solution hardening effect in terms of pinning would require the dislocation configuration to be of a smoothly bowed, line-tension type.

This is in accordance with the transmission electron microscope observations of Laister and Jenkins,[13] who found bowed arrays for undoped GaAs after deformation at 800 °C. The plateau behavior for undoped GaAs in Fig. 2 would then be associated with pinning caused by dislocation intersections, residual impurities, jogs, or antisite defects. Alternatively, another solid solution hardening effect could be applicable. If dislocation motion occurred by double kink nucleation and growth, solute hardening would be manifested through a retardation of the growth step of lateral kink propagation, with the kink pinning effect still being proportional to δV. The similar plateau behavior for GaAs with and without In would then be a logical consequence since the same detailed mechanism of dislocation motion would be appropriate for both cases. Deformation of GaAs at the low temperatures of 320 °C and 400 °C does give straight dislocations[14,15] consistent with a double kink model and the interpretation of the first stage of deformation in Fig. 1. We plan to undertake transmission electron microscope studies of the deformed alloys to determine whether the plateau region specimens correspond to bowed or straight dislocations to decide which of the above models is applicable. In the context of the present work, however, either model corresponds to a solid solution hardening effect of In.

Hardness is approximately equal to three times the lower yield stress.[9] Moreover, the critical resolved shear stress (CRSS) equals the yield stress times the Schmid factor of about 0.5.[16] Thus, the CRSS is approximately equal to H/6. The CRSS obtained from hardness data is presented as a function of temperature in Figure 3. The hardness to flow stress conversion is presented only for temperatures above 400°C where

no cracking at indentation corners is observed and significant plastic flow occurs. For comparison, also shown are CRSS data from compression tests on undoped Bridgman crystals by Swaminathan and Copely[17] and on undoped and In-doped LEC crystals by Tabache,[18] both of which also represent values for the lower yield stress. The greater strength of the present crystals with no In doping may be associated with the presence of boron. Boron, an isoelectronic substitution for gallium, would produce a larger size mismatch, $\delta V/V$ ~50%, than In, but an attendant lower solubility. Hence, it should also be a strong hardener if uniformly distributed in solution, an effect verified experimentally,[1] but could lead to internal stresses and dislocation generation if present in an inhomogeneous distribution or as precipitates.

Extrapolation of data from the present work, for the undoped and highly doped cases, to the melting point T_m gives CRSS values of 15 and 23 MPa respectively. The dislocation content and the resolved shear stress caused by thermal stresses experienced during crystal growth varies across the diameter according to the conventional W form.[3,10] The maximum resolved shear stresses calculated[3,19,20] to arise from thermal stresses at temperatures near T_m during crystal growth are 20 MPa in the central region and rise to 50 MPa at the crystal edges. It must be pointed out here that CRSS values obtained from hardness measurements are upper bound estimates and the extrapolation to the melting point is made with some reservation because there is most likely an intervening change in the deformation mechanism as discussed later. However, the present results suggest that crystals highly doped with In and containing B may have sufficient solid solution hardening to

prevent yielding during crystal growth at least in the center. Further work is needed to resolve the difference between the present results and the compression test results in Fig. 3, in particular with respect to the possible role of boron.

While the above results would suffice to explain the suppression of dislocation formation by means of In additions, the extrapolation of the plateau data to the melting point is questionable, because there is most likely an intervening change in the deformation mechanism. Since GaAs has a structure similar to Si and the deformation map for GaAs is not available at the present time, the Si deformation map[21] is used here as a guideline for this possible transition in mechanism. Figure 4 presents data extracted from the Si map for strain rates of 10^{-3} to 10^{-7} s^{-1}. The flow behavior undergoes a transition from flow following the double kink model to that of a power law creep model at about $0.5T_m$. For GaAs, the intervention of solid solution hardening is expected to move the transition to power law creep to higher homologous temperatures, but, on the basis of all available deformation map data[21] to still leave a region of power law creep below the melting point. The cellular dislocation networks present in as-grown GaAs crystals with dislocation densities of the order of 10^3-10^4 cm/cc provide indirect evidence that climb processes are involved in the deformation occurring during crystal growth. As indicated in Fig. 4, the transition to power law creep at a given strain rate and temperature is less than that for double-kink flow extrapolated to the same conditions. However, even for the power law creep region, In can have a hardening influence.

In the region of power law creep, the dislocation velocity, and

hence, the flow stress level would depend on the lattice interdiffusion coefficient or diffusivity. In this regime, the dislocation velocity for a given applied stress is given by[21]

$$v \approx \frac{D_v \sigma_n \Omega}{b K T}$$

Here D_v is the bulk diffusivity, σ_n is the local normal stress that produces a climb force on the dislocation, k is Boltzmann's constant and Ω is the atomic volume. Because σ_n is proportional to the flow stress σ_s and the average dislocation velocity is proportional to the strain rate $\dot{\epsilon}$, the latter is given by[21]

$$\dot{\epsilon} \approx \frac{A D_v \mu b}{k T} \left[\frac{\sigma_s}{\mu}\right]^3$$

where μ is the shear modulus, A is a dimensionless constant, and b is the length of the Burgers vector. For a binary compound, D_v is replaced by $D_{eff}=D_{Ga}D_{As}/D_{Ga}+D_{As}$.[21] Thus, the stress for a given strain rate would be controlled in the GaAs lattice by the slower of the diffusing species which is arsenic. The influence of solute elements on the diffusion in the arsenic sublattice would thus be an important factor in determining the effect of solute elements on the deformation behavior. The trapping of arsenic vacancies because of elastic interactions or electronic interactions with In solute centers would be a possible factor that could reduce D_{eff}, and hence, provide a hardening effect in the power law creep regime.

At high temperatures, where solute atoms are mobile, resistance to dislocation motion also comes from the drag of a solute atmosphere by

the dislocation. The force-velocity relationship for this Cottrell drag has been treated in detail.[22] For a given dislocation velocity v, the drag stress increment caused by the solute atmosphere varies as the square of the strength of solute-dislocation interaction δV and inversely as the effective diffusivity. The solute drag stress versus temperature curve would exhibit a maximum and if present,would be superposed on the strength versus temperature plot as shown by the dotted line in Fig. 1. Because of very low diffusivities in the GaAs lattice, the solute drag effect is expected at quite high temperatures.

All of the preceding discussion has been in terms of quasi-steady state flow corresponding to deformation at and subsequent to the lower yield point. An additional hardening-type influence of In could be manifested if the deformation during crystal growth occurred mainly in the transition region reflected by the microyield stress, the upper yield point and deformation between the upper and the lower yield points. A retarding effect of In on dislocation motion during multiplication would tend both to increase the upper yield point and to prolong the strain range between the upper and lower yield points.[23,24] The microyield stress, at which dislocation motion begins, would also be increased by such a retarding effect.

Thus while the plateau stress data extrapolated from 900°C indicates sufficient hardening to suppress flow on the basis of estimated thermal stresses, other hardening or softening effects associated with different deformation mechanisms above 900°C could be present. Such mechanisms are expected on the basis of theory. We are

presently extending the deformation work to temperatures above 900 ^{o}C where conventional indentation methods are inapplicable.

SUMMARY

High temperature hardness tests at up to 900 ^{o}C of undoped and In-doped GaAs showed an appreciable strengthening effect of In in GaAs. The existence of an athermal, plateau stress region is indicated for the three alloys. The GaAs containing In shows a higher plateau stress level compared to GaAs with no In. Calculations suggest that the hardening produced by indium may be sufficient to exceed the thermal stress experienced by the crystal during growth. However studies, at higher temperatures are needed to resolve the possibility of a change in the deformation mechanism near the melting point. Strengthening at higher temperatures with In additions is consistent with a solution hardening model for dislocation density reduction in In-doped GaAs.

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ACKNOWLEDGEMENTS

The authors are grateful for the support of this work by the Defence Advanced Research Projects Agency (DOD), DARPA Order No. 5526, monitored by AFOSR under Contract # F49620-85-C-0129, and for the help of R.N. Thomas and other members of the Devices Group at the Westinghouse R&D Center, for providing materials for this research under their contract with DARPA # DARPA-Westinghouse-N-00014-84-C-0632 as well as for contributing helpful discussions.

Table I. Hardness data for all three alloys as a function of temperature.

TEMPERATURE	HARDNESS (GPa)		
C	GaAs	$Ga_{0.9975}In_{0.0025}As$	$Ga_{0.99}In_{0.01}As$
25	5.82 ±0.2	5.82 ±0.2	5.92 ±0.22
100	5.52 ±0.16	5.39 ±0.15	5.26 ±0.2
200	3.50 ±0.3	3.41 ±0.21	3.65 ±0.1
300	2.23 ±0.15	2.13 ±0.18	2.14 ±0.25
400	1.20 ±0.03	1.33 ±0.04	1.19 ±0.06
500	0.72 ±0.02	0.76 ±0.04	0.79 ±0.01
600	0.52 +0.03	0.58 ±0.014	0.64 ±0.013
700	0.38 ±0.014	0.45 ±0.015	0.49 ±0.03
800	0.291±0.01	0.324±0.01	0.38 ±0.01
900	0.21 ±0.01	0.26 ±0.01	0.293±0.01

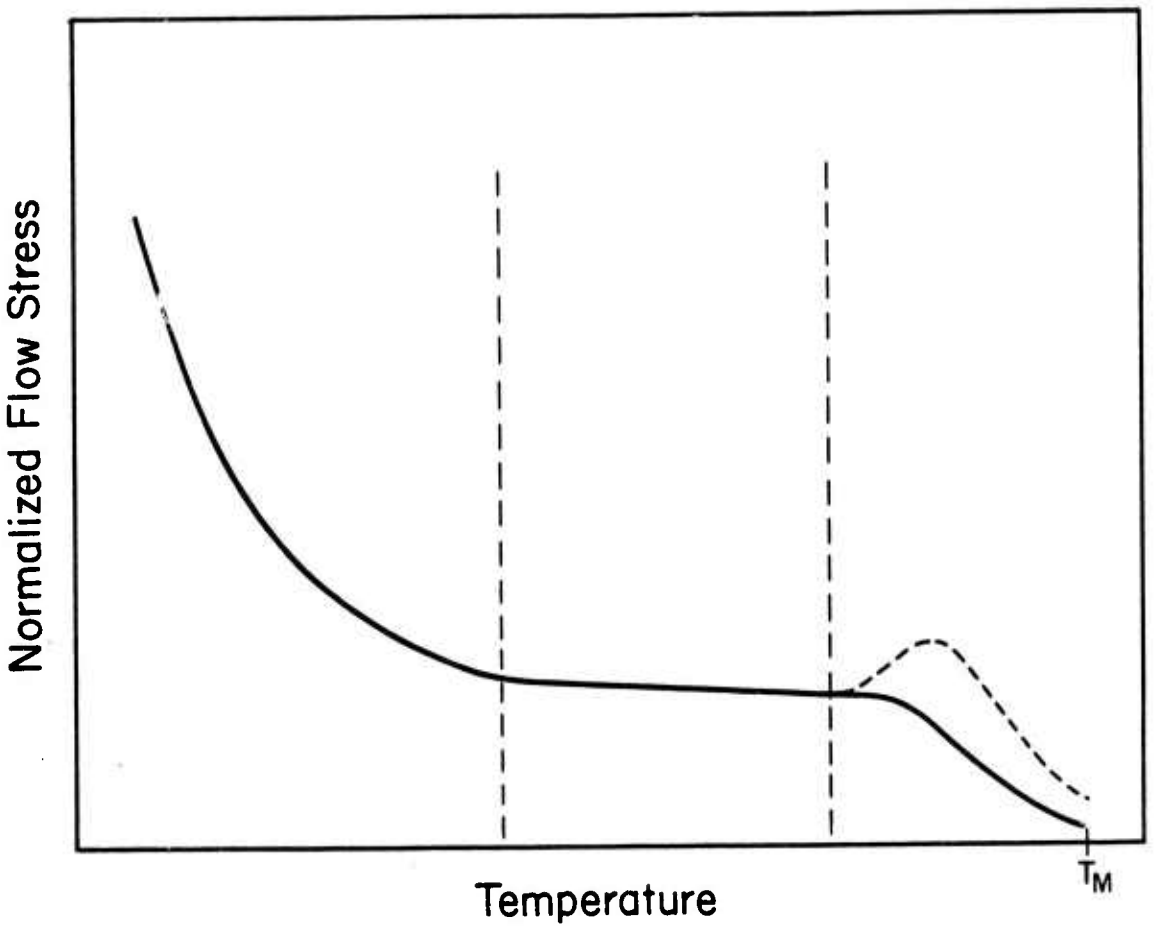
Figure Captions

Figure 1. Schematic normalised flow stress versus temperature curve for GaAs at a constant strain rate.

Figure 2. Normalised hardness versus temperature plot for GaAs, $Ga_{0.9975}In_{0.0025}As$ and $Ga_{0.99}In_{0.01}As$.

Figure 3. Critical resolved shear stress estimated from hardness data compared with the compression test data of Swaminathan and Copely[17] on undoped GaAs and of Tabache[18] on undoped and In-doped LEC GaAs.

Figure 4. A section of deformation mechanism map of Si which belongs to the same iso-mechanical group as GaAs.[21]



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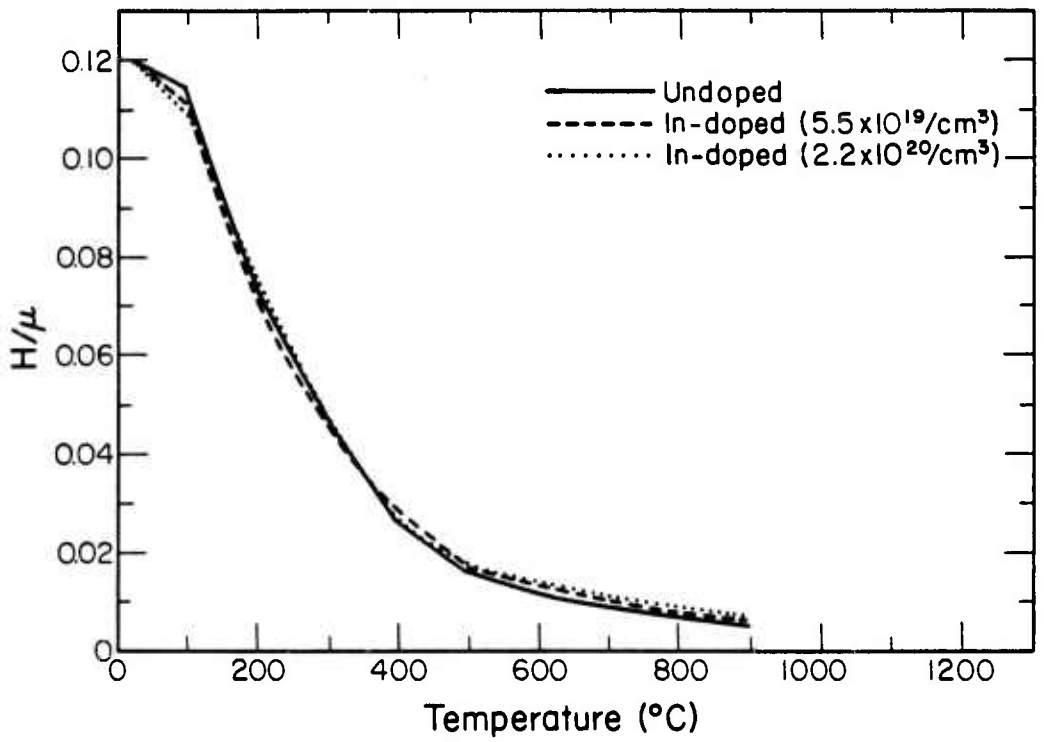
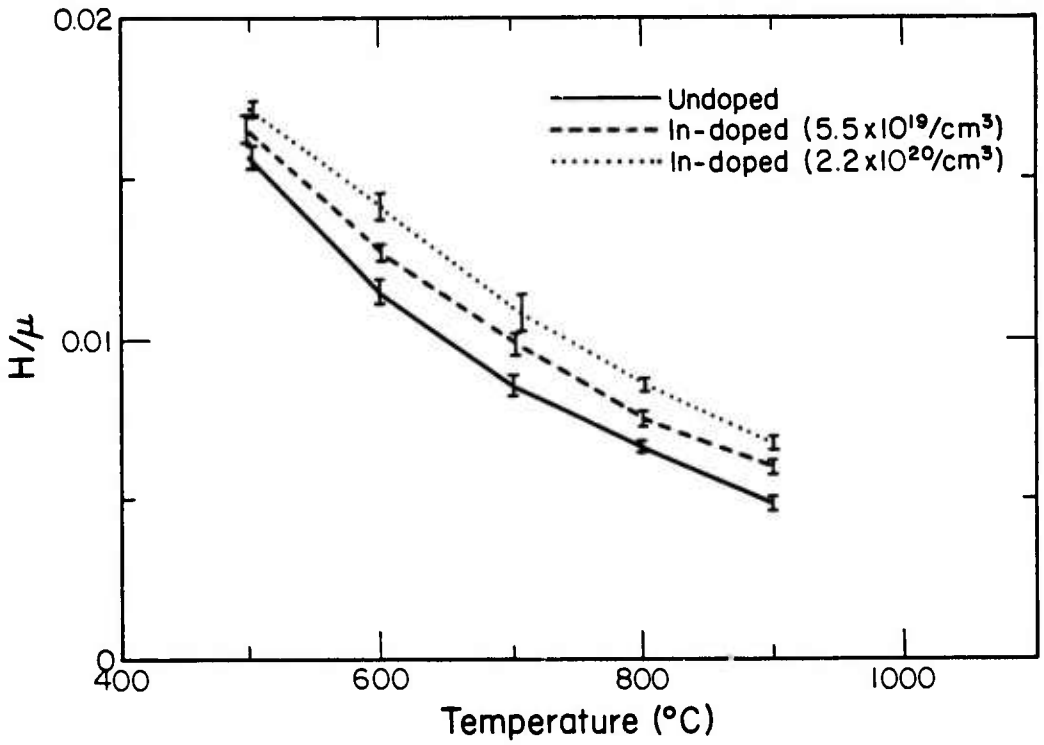
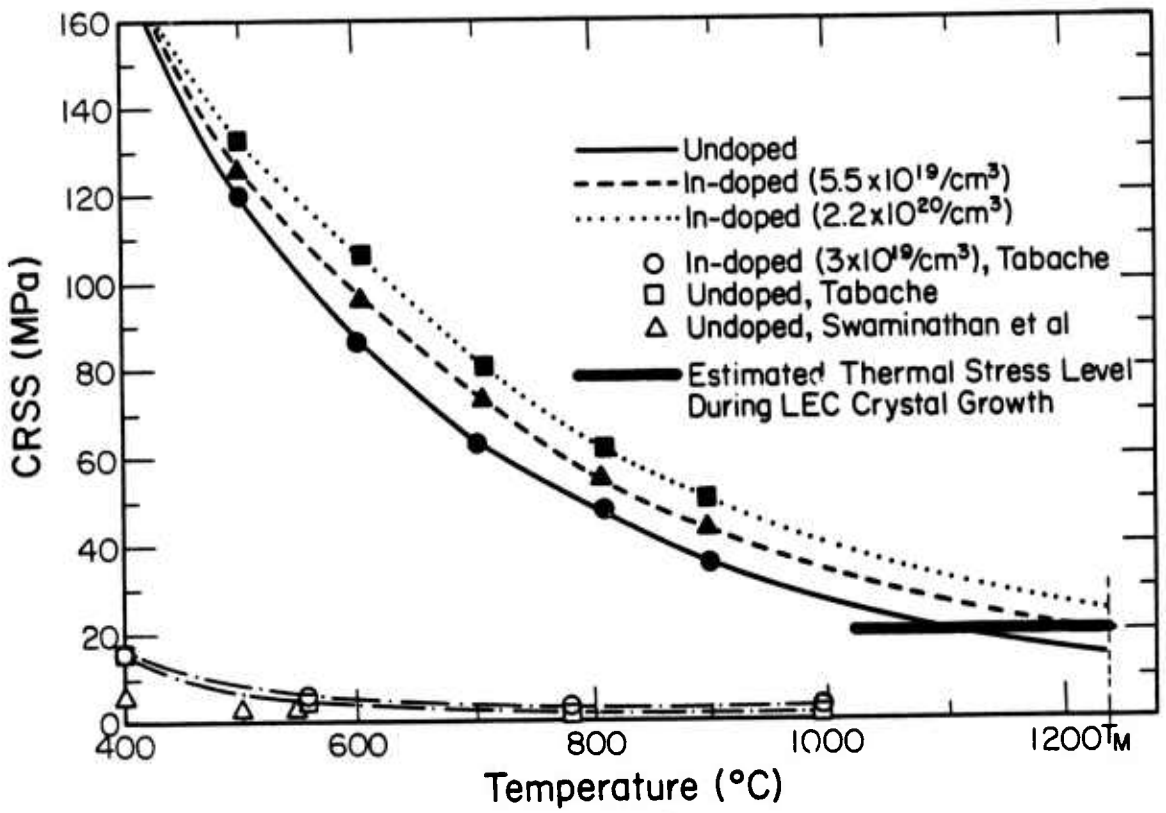


(a)



(b)

Figure 2. Normalised hardness versus temperature plot for GaAs, $Ga_{0.9975}In_{0.0025}As$ and $Ga_{0.99}In_{0.01}As$.



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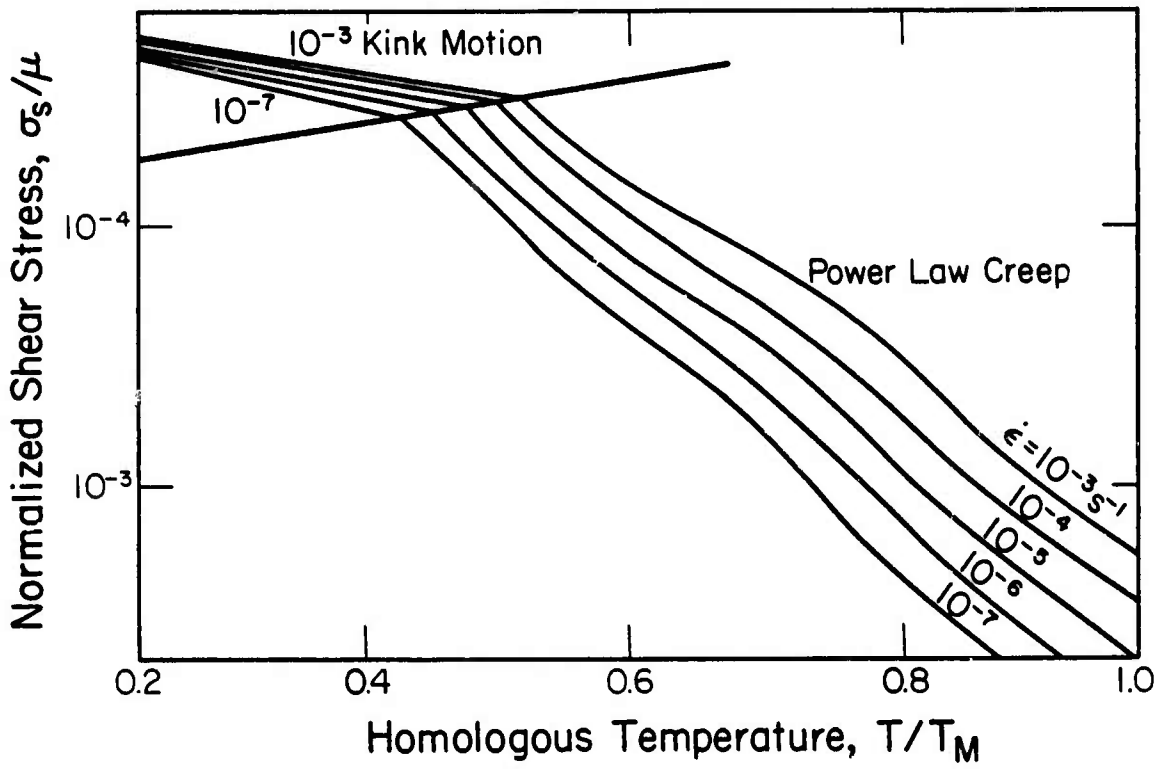

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